# Isotopic tracers and the fate of dissolved carbon in natural and artificial water systems

**PAULA NIINIKOSKI**

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Cover photo: Erno Sjögren. Back cover photo: Tobias Fusswinkel.

Author´s address: Paula Niinikoski
Department of Geosciences and Geography
P.O.Box 64
00014 University of Helsinki
Finland
paula.niinikoski@helsinki.fi

Supervised by: Professor Juha Karhu
Department of Geosciences and Geography
University of Helsinki

Reviewed by: Professor Emeritus Ramón Aravena
Department of Earth and Environmental Sciences
University of Waterloo

Professor Marja Tiirola
Department of Biological and Environmental Science
University of Jyväskylä

Opponent: Professor Rama V. Krishnamurthy
Department of Geosciences
Western Michigan University

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## Abstract

Access to clean water is a growing global concern, and understanding all the different processes affecting the quantity and quality of both surface and groundwater is crucial to meeting this increasing demand for water. Information on the carbon contents of surface water systems is also essential for understanding the carbon balance of the entire atmosphere. Whether surface waters serve as a source or a sink of carbon can have an effect on atmospheric changes in $CO_2$ at a global scale. Better knowledge of the carbon cycle in rivers is, therefore, an important part of preparing for changes due to the increase in the $CO_2$ concentration of the atmosphere. In addition, studying the carbon contents of river water increases our understanding of the vulnerability of catchments, and helps to enhance the quality of drinking water.

Stable isotopes are natural tracers. The stable isotopic composition of oxygen and hydrogen in water can be used to monitor the travel times and routes of surface and groundwater by utilising the fractionation effects caused by temperature on precipitation, and evaporation on surface water. The isotopic composition of dissolved inorganic carbon in the river water can be used to investigate the origin of carbon, which provides implications for the organic and inorganic processes transferring carbon into the water.

In this study, stable isotopes are utilized together with multiple chemical analyses and modelling methods to further understand the processes that control the hydrosphere. The two main aims are: 1) to establish the conditions under which the stable isotopic composition of hydrogen and oxygen in water can be used to determine mean residence times (MRT), and 2) to better understand the processes controlling the dissolved carbon contents in artificial and natural water systems, in order to use this understanding to help maintain and improve the quality of the water.

The study sites included two rivers, the Vantaanjoki and the Kokemäenjoki River, in southern and southwestern Finland, respectively, and a managed aquifer recharge (MAR) site at Virttaankangas in southwestern Finland. The mean residence time of water was determined for both rivers and the MAR site using the isotopic composition of oxygen in water. The results suggested that isotope based MRT determination is applicable in simple systems with known water sources. This was the case for the Vantaanjoki River, where the water mainly comes from two distinct sources: base flow and surface flow during spring flooding. The mean residence time of the snow cover, and the water in the flooding event, could be determined by the isotope method. The base flow component was too old to be dated by this method. At the Virttaankangas MAR site, the two known components were local groundwater and infiltrated water, the latter being suitable for MRT determination.

The carbon budget of the Vantaanjoki River showed signs of both base flow influence and photosynthesis and decay taking place in the river channel. Human induced changes played a minor role in the inorganic carbon balance. Decay of organic material could also be perceived at

Virttaankangas MAR site, where the organic matter in the infiltrated water is microbially decomposed into inorganic form. This process could be monitored by combining the isotopic technique with geochemical modelling. The beginning of the decomposition was delayed compared to most MAR sites, which may be due to an uncommonly high pH of the water in the aquifer, caused by calcite dissolution.

These results confirm that there are many applications for isotopic methods. The annual isotope signal in precipitation is a good tool for determining the MRT, especially in two component systems. The isotopic composition of DIC, together with that of oxygen and hydrogen, can be applied to study surface flow –base flow interaction in river catchments. Oxidative decomposition of DOC in MAR can be monitored using $\delta^{13}C_{DIC}$ together with geochemical modelling in cases where there are other sources contributing to the DIC.

# Tiivistelmä


Puhtaan veden saatavuuden turvaaminen on kasvava globaali huolenaihe. Veden laatuun ja määrään vaikuttavien prosessien ymmärtäminen onkin avainasemassa, kun kasvavaan kysyntään yritetään vastata. Pintavesien hiilitase vaikuttaa koko ilmakehän hiilitaseeseen ja tätä kautta ilmastonmuutokseen joko sitä hidastavasti tai kiihdyttävästi, joten sen vaikutukset yltävät paikallisista maailmanlaajuisiin. Näin ollen vesistöissä tapahtuvan hiilen kiertokulun ymmärtäminen auttaa valmistautumaan ilmakehän kasvavan hiilidioksidikuorman aiheuttamiin muutoksiin. Lisäksi hiilen kiertokulku jokisysteemeissä antaa tietoa valuma-alueiden haavoittuvuudesta ja helpottaa juomaveden laadun seurantaa ja parantamista.

Stabiilit isotoopit ovat luonnollisia merkkiaineita. Hapen ja vedyn isotooppikoostumusta voidaan käyttää veden viipymän ja kulkeutumisreittien selvittämisessä tutkimalla lämpötilan ja haihtumisen aiheuttamaa fraktioitumista. Liuenneen epäorgaanisen hiilen isotooppikoostumusta voidaan puolestaan hyödyntää hiilen lähteen selvittämiseen, mikä auttaa ymmärtämään hiiltä veteen tuottavia orgaanisia ja epäorgaanisia prosesseja.

Tässä tutkimuksessa stabiileja isotooppeja on käytetty yhdessä kemiallisten analyysimenetelmien ja mallinnuksen kanssa tavoitteena hydrosfäärissä tapahtuvien prosessien parempi ymmärtäminen. Tutkimuksen kaksi päätavoitetta olivat: 1) määritellä reunaehdot tilanteille, joissa hapen ja vedyn isotooppikoostumusta voidaan käyttää onnistuneesti veden keskimääräisen viipymän selvittämiseen, ja 2) tuottaa tietoa keinotekoisten ja luonnollisten vesijärjestelmien hiilitaseen ymmärtämiseksi auttamaan veden laadun parantamisessa ja valvonnassa.

Tutkimuksen kohteina oli kaksi jokea, Vantaanjoki ja Kokemäenjoki, Etelä- ja Lounais-Suomessa, sekä Virttaankankaan tekopohjavesilaitos Lounais-Suomessa. Veden keskimääräinen viipymä määritettiin molemmista joista sekä tekopohjavesilaitoksen imeytysvedestä käyttäen hapen stabiileja isotooppeja. Tuloksista kävi ilmi, että menetelmä toimii yksinkertaisissa vesistöissä, joissa veden muodostavat komponentit tunnetaan hyvin. Tällainen tilanne on esimerkiksi Vantaanjoessa, jossa jokivesi muodostuu kahdesta komponentista: pohjavedestä sekä kevättulvan kuljettamasta pintavalunnasta. Tässä tapauksessa laskettu kesimääräinen viipymä kuvastaa lumipeitteen viipymää eteläisessä Suomessa. Jokiveden pohjavesikomponentti on liian vanha tällä menetelmällä ajoitettavaksi. Virttaankankaan tapauksessa kaksi tunnettua komponenttia olivat luonnollinen pohjavesi ja imeytetty tekopohjavesi. Näistä jälkimmäisen keskimääräinen viipymä oli mahdollista selvittää isotooppimenetelmää käyttäen.

Vantaanjoen hiilitaseessa näkyivät sekä pohjavesivaikutus että yhteyttämisen ja hajoamisen vuosittainen sykli. Ihmistoimet näkyivät epäorgaanisessa hiilitaseessa ainoastaan erittäin paikallisesti. Myös Virttaankankaalla mikrobien aiheuttama orgaanisen aineksen hajoaminen näkyi liuenneen epäorgaanisen hiilen koostumuksessa. Tämän prosessin seuraamiseksi oli isotooppimenetelmä yhdistettävä geokemialliseen mallinnukseen. Orgaanisen aineksen hajoamisen alku oli Virttaankankaalla viivästynyt muihin tekopohjavesilaitoksiin verrattuna, mahdollisesti kalsiitin liukenemisen aiheuttamasta epätavallisen korkeasta pH:sta johtuen.

Tulokset vahvistavat, että isotooppimenetelmille on paljon käyttöä. Sadannan isotooppikoostumuksen vuosittaiset vaihtelut ovat hyvä keino selvittää keskimääräinen

viipymä soveltuvissa, kahden komponentin vesissä. Liuenneen epäorgaanisen hiilen isotooppikoostumus, yhdessä hapen ja vedyn kanssa, auttaa selvittämään pinta- ja pohjaveden välisiä vuorovaikutuksia vesistöissä. Liuenneen orgaanisen hiilen hajoamista tekopohjavesilaitoksilla voidaan seurata yhdistämällä isotooppimenetelmät geokemialliseen mallinnukseen tapauksissa, joissa useammat lähteet vaikuttavat liuenneen epäorgaanisen hiilen isotooppikoostumukseen.

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# Contents

## List of original publications

This thesis is based on the following publications:

I Niinikoski P., Hendriksson N.M. and Karhu J.A. 2016. Using stable isotopes to resolve the effects of water storage in aquifers and lakes on the residence time of river water. Isotopes in Environmental and Health Studies 52, 380-392.

II Niinikoski P., Saraperä S., Hendriksson N.M. and Karhu J. A. 2016. Geochemical and flow modelling as tools in monitoring managed artificial recharge. Applied Geochemistry 74, 33-43.

III Niinikoski P. and Karhu J. A. Natural vs. anthropogenic effects in the composition of dissolved inorganic carbon in a boreal river with a seasonal base flow component. Submitted to Hydrology Research.

The publications are referred to in the text by their roman numerals.

Author's contributions to the publications:

I The study was planned by all authors. Sampling at the Vantaanjoki River and analysis of the samples was executed by P. Niinikoski as was the modelling involved. P. Niinikoski also prepared the manuscript.

II The study was planned by all authors. P. Niinikoski was responsible for DIC isotope analysis, geochemical modelling and she also prepared the manuscript.

III The study was planned by both authors. Sampling and analysis was executed by P. Niinikoski, who also prepared the manuscript.

## Abbreviations

DIC Dissolved inorganic carbon
DOC Dissolved organic carbon
MAR Managed aquifer recharge
MRT Mean residence time
STT Shortest travel time

## List of tables and figures

# 1. Introduction

Water is one of the most important natural resources, and access to clean water is a growing global concern (Gale, 2005). Water sources and procedures to acquire the necessary water for the needs of the population differ significantly. Therefore, understanding all the different processes affecting the quantity and quality of both surface and groundwater is crucial to meeting this increasing demand for water.

Knowledge of the carbon contents of surface water systems is an important element for understanding the carbon balance of the atmosphere. Whether surface waters serve as a source or a sink of carbon can have an effect on changes in the contents of atmospheric $CO_2$ at a global scale (Toggweiler 1995; Telmer and Veizer 1999). In addition, this improves our understanding of the vulnerability of catchments. In water supply systems, organic matter allows unwanted bacterial growth leading to odour, taste or even health problems (Miettinen et al. 1999; Lindroos et al. 2002). Potential risks may also arise, if dissolved organic carbon (DOC) in water supply system is affected by chlorine disinfection, potentially leading to the formation of mutagenic or carcinogenic compounds (Lindroos et al. 2002).

In this study, stable isotopes are utilized together with chemical and physical analyses and modelling methods to increase our understanding of the processes in the hydrosphere. Hydrogen and oxygen isotopes are especially useful for studying fragile natural environments or waters used for human consumption, since they are part of the water molecule and the methods are not dependent on additional dissolved tracers.

## 1.1 Isotope tracers

### 1.1.1 Definitions

Isotopic composition changes are calculated as δ values from isotopic ratios (the abundance of the heavier isotope divided by that of the lighter isotope):

$$\delta_{sample} = R_{sample} / R_{std} - 1$$

where $R_{sample}$ is the isotope ratio in the sample and $R_{std}$ is the same isotope ratio in a standard (Coplen, 2011). The δ values are given in permille. For hydrogen and oxygen in water, the applicable standard is Vienna Standard Mean Ocean Water (VSMOW) and for carbon it is Vienna PeeDee Belemnite (VPDB).

### 1.1.2 Hydrogen and oxygen in water

The stable isotope ratios of oxygen and hydrogen have many potential applications in hydrogeology. For instance, they can be used to examine interactions between groundwater and surface water, and to estimate the mean residence time of water in the catchment (Stadnyk et al., 2005; Burgman et al., 1987; Reddy et al., 2006; Broxton et al., 2009).

In temperate regions close to the poles the isotopic composition of precipitation depends primarily on the mean annual temperature of the locality. Lower mean temperatures produce precipitation that is depleted in $^{2}H$ and $^{18}O$ compared to regions with higher mean annual temperatures (Dansgaard, 1964; Rozanski et al., 1982; Kurita et al., 2004; Gat, 1996). In temperate regions, also seasonal temperature variations are reflected in the isotopic composition of precipitation. In the warm months of the summer the isotopic composition of precipitation is enriched in $^{2}H$ and $^{18}O$ compared to colder winter months (Rozanski et al., 1982; Gat, 1996; Kortelainen and Karhu, 2004; Bowen 2008). As a result, the stable isotope composition of

precipitation shows a sinusoidal pattern with a period of one year.

Dansgaard (1964) defined the Global Meteoric Water line (GMWL) as a line describing the isotopic composition of water in global precipitation:

$$\delta^2H = 8\times\delta^{18}O + 10\ (‰)$$

On the basis of a long term monitoring of 219 precipitation collection sites across the world Rozanski et al. (1993) found the following relationship for the connection between $\delta^2H$ and $\delta^{18}O$:

$$\delta^2H = 8.17\times\delta^{18}O + 11.27\ (‰)$$

For local variability, a better reference line is a local meteoric water line (LMWL), which is based on precipitation in the study region. Kortelainen and Karhu (2004) concluded that the LMWL for Finland is:

$$\delta^2H = 7.84\times\delta^{18} + 9.35\ (‰)$$

Evaporation changes the isotopic composition of water. The fractionation of isotopes through evaporation favours the loss of lighter isotopes hence the remaining water is enriched in heavier isotopes (Dansgaard, 1964; Gat, 1996). Note that due to differing atomic masses, the loss of the lighter isotope affects the $\delta^{18}O$ values more than $\delta^2H$ values. This process drives the composition of evaporated samples below the LMWL.

The distance of the sample from the GMWL can be expressed through the d-excess value (Dansgaard 1964). D-excess is calculated from the $\delta^{18}O$ and $\delta^2H$ values by the formula:

$$\text{d-excess} = \delta^2H - 8\times\delta^{18}O\ (‰)$$

A d-excess of 10‰ is expected for average global precipitation, although it can vary regionally due to differences in humidity, wind speed, and sea surface temperature (Clark and Fritz, 1997). In evaporated samples, the d-excess value tends to be lower than in precipitation (Dansgaard 1964).

### 1.1.3 Dissolved inorganic carbon

The dissolved inorganic carbon (DIC) in surface and groundwaters carries with it an isotopic signal inherited from the source of the carbon. Three sources of carbon can be identified from the isotopic composition of DIC:

1. Biogenic carbon is produced by photosynthetic fixation. Biogenic processes preferentially favour the lighter carbon isotope; thus, organic material is depleted in the heavier isotope (Telmer and Veizer 1999; Barth and Veizer 1999). Quantitatively, this translates to a $\delta^{13}C$ value of approximately -27‰ (Deines 1980, Vogel 1993, Schiff et al. 1997). As microbes oxidatively decompose organic carbon to form DIC, the isotopic composition of total DIC shifts towards values more depleted in the heavier carbon isotope (Barth and Veizer 1999). The opposite effect occurs in photosynthesis because it removes lighter carbon from the DIC, enriching the remaining DIC in the heavier isotope (Telmer and Veizer 1999).

2. Atmospheric carbon has a $\delta^{13}C$ value of approximately -8‰ (Keeling et al., 2005). Equilibration with the atmosphere leads to $\delta^{13}C_{DIC}$ values of approximately 0‰ (Barth and Veizer, 1999). If the partial pressure of $CO_2$ in surface water is lower than that in the atmosphere, the surface water can take up carbon from the atmosphere (Keeling et al., 2005). Conversely, a higher than the atmospheric partial pressure of $CO_2$ leads to escape of carbon from the water (Doctor et al. 2008; Butman and Raymond 2011; Wallin et al. 2012). The lighter carbon is more

readily lost into the atmosphere, hence leaving the residual more enriched in the heavier isotope (Keeling et al., 2005; Doctor et al. 2008; Van Geldern et al. 2015).

3. Carbon derived from the dissolution of carbonate minerals can vary in isotopic composition, depending on the source. For example, the calcite derived from the Satakunta Sandstone Formation, found in the Virttaankangas esker, have a $\delta^{13}C$ value of approximately -4.8 ±0.5‰ (Kortelainen et al., 2007). Carbonate minerals from marine sedimentary deposits generally have $\delta^{13}C$ values close to 0‰ (Keith and Weber, 1964).

## 1.2 Applications in hydrology

### 1.2.1 Determining mean residence time

The seasonal variation of the isotope ratios in precipitation can be inherited by river and/or by groundwater (Gat 1996; Kendall and McDonnell 1998; Kortelainen and Karhu 2004). The inheritance of isotopic composition can be utilized to determine the mean residence time (MRT) of the water, by fitting a sinusoid function to the isotopic signal in the precipitation and the studied water body (Stichler 1980; Burgman et al. 1987; Clark and Fritz 1997). There are two simple methods for evaluating the MRT from these functions: the amplitude damping method and the phase shift method (Burgman et al., 1987; Dóša et al., 2011). Amplitude damping occurs because older and younger waters mix in the reservoir resulting in flattening of the isotope signal with time, making the fluctuations disappear within three years (Clark and Fritz, 1997). A phase shift in the signal occurs through retention of the isotope signal, not through mixing of isotopic compositions. The following relationships can be applied to determine the MRT:

For the amplitude damping method:

$$MRT = ½\ \pi\ (1\text{-}C)^{1/2} / C$$

where C is the amplitude damping given as C=B/A. Here A is the amplitude of the $\delta^{18}O$ values in precipitation and B that of the $\delta^{18}O$ values in river water (Burgman et al., 1987). For the phase shift method:

$$MRT = \tan(\alpha/2\pi)$$

where $\alpha$ is the phase displacement and the full phase is $2\pi$ (Stichler et al., 1980).

These methods, however, can provide erroneous results. This was shown by Kirchner (2015) for catchments where water is from different sources with different mean residence times. Thus, different sinusoidal signals of the isotopic composition are incorporated in the mixed catchments producing a composite curve that cannot be resolved using the above relationships (Kirchner et al. 2010; Stewart et al. 2010; Kirchner 2015). However, these methods give correct results in simple one component systems, but they should be used with care.

### 1.2.2 Groundwater - surface water interaction

The changes in the isotopic composition of water caused by evaporation can be used to differentiate between surface and groundwater, since groundwater generally does not undergo significant evaporation (Gat, 1996). Especially, this has been demonstrated to be true in temperate regions (Kortelainen and Karhu, 2004). Therefore, the effect of surface water seeping into the groundwater can be detected either by comparing the groundwater composition against the LMWL or GMWL, or by calculating the d-excess. The opposite process, in which groundwater discharges into the surface water

may be more difficult to detect by isotopic methods.

Damping of the isotopic signal, described in section 1.2.1., can be due to storage of water in large surface water bodies or as groundwater. Differentiating between the two can be done by comparing the annual means of the isotopic composition of either oxygen or hydrogen in precipitation and in the surface or groundwater in question (Dansgaard 1964). If the annual means are equal, no significant evaporation has occurred and the damping of the isotopic signal is caused by storage as groundwater, instead of storage in lakes. If, however, the annual means differ significantly, evaporative effects in lakes can be suggested. The degree of evaporation can be evaluated by plotting the $\delta^{18}O$ and $\delta^{2}H$ values and comparing them to the LMWL.

Quantifying the amount of evaporated surface water in groundwater can be achieved by a simple isotope mass balance calculation, if the isotopic compositions of the surface water, and unaffected groundwater in the area are known:

$$\delta^{18}O_{sample} = f \times \delta^{18}O_{gw} + (f-1) \times \delta^{18}O_{sw}$$

The same mixing calculation can generally not be applied to surface waters, because there often are too many endmembers.

### 1.2.3 Monitoring managed aquifer recharge

Replenishing groundwater reserves with surface water by managed aquifer recharge (MAR) is a technique to maintain groundwater resources (Freeze and Cherry, 1979; Asano, 1985; Ma and Spalding, 1997; Gale, 2005; Dillon, 2005; Page et al., 2012; Dillon, et al., 2009). In addition to serving as water storage, MAR also helps in treating the infiltrated water for impurities (Grove and Wood, 1979; Artimo et al., 2003; Kortelainen and Karhu, 2006).

Water purification by MAR is most commonly done to lower the contents of DOC in the infiltrated water (Sundlöf and Kronqvist 1992; Hatva 1996; Van Breukelen et al. 1998; Kuehn and Mueller 2000; Lindroos et al. 2002; Balderer et al. 2004; Grünheid et al. 2005; Kortelainen and Karhu 2006; Kolehmainen et al. 2009). This is achieved by both microbially induced oxidative decomposition in the aquifer and by sorption (Frycklund 1995; 1998; Kortelainen and Karhu 2006; Kolehmainen et al. 2009). The decomposition of DOC produces DIC with an isotopic composition typical of biogenic carbon (Le Gal La Salle et al., 2005; Kortelainen and Karhu, 2006; Kolehmainen et al., 2010). Therefore, the amount of DOC reduction contributed to decomposition can be deduced by simple isotope mass balance calculations, assuming there are no other sources of carbon contributing to the DIC pool. If there are other sources of DIC, such as carbonate dissolution, more complex geochemical modelling is required to differentiate between the sources.

## 1.3 Aims of this study

In this study, stable isotope tracers were combined with geochemical and flow modelling to obtain a better understanding of the processes which affect carbon cycling in naturally occurring and artificial water systems. Information on transit times of water in different environments has been integrated in order to study the evolution of the carbon contents in water. This was achieved predominantly through investigating the isotopic composition of oxygen and hydrogen in water, and the isotopic composition of carbon in DIC. Analytical data was combined using geochemical and flow modelling.

More specifically, the aims of this study were:

1. To investigate the circumstances under which the sinusoidal function fitting can provide

**Table 1.** Landuse and size of the catchments of the Vantaanjoki and the Kokemäenjoki rivers.

| | Vantaanjoki River | Kokemäenjoki River |
|---|---|---|
| Catchment size km$^2$ | 1 700 | 27 000 |
| Lake % | 3 | 11 |
| Agriculture % | 36 | 23 |
| Forest % | 41 | 60 |
| Peatland % | 0 | 6 |
| Urban and industrial % | 20 | 0 |
| Mean annual discharge m$^3$/s | 16 | 180 |
| Maximum discharge m$^3$/s | 200 | 300 |

credible results for the estimation of the mean residence time (papers I and II).

2. To use isotopic methods in quantifying groundwater - surface water ratios in a base flow affected river, and to investigate, if groundwater - surface water interaction and human induced changes have an effect on the composition of dissolved inorganic carbon in river water (papers I and III).

3. To follow the initiation of a managed aquifer recharge process, and to pinpoint the onset and quantify the amount of DOC reduction, the proportion of oxidative decomposition and the resulting water quality in a high pH environment (Paper II).

# 2. Study sites

## 2.1 Vantaanjoki and Kokemäenjoki rivers

The Vantaanjoki River is located in the most densely populated area in Finland, whereas in the catchment of the Kokemäenjoki River urban areas are scarce (Table 1). Geographically, the two rivers are not far apart, located in southern and southwestern Finland, respectively (Fig. 1). The bedrock of both catchments contains Precambrian granitoids and gneisses, with overlying Quaternary glacial deposits (Tikkanen, 1989; Ehlers et al., 1995; Korsman et al., 1997; Ehlers and Gibbard, 2004; Konsala et al. 2008). In the Vantaanjoki River catchment, interaction between surface water and groundwater has been reported in previous studies (Korkka-Niemi et al., 2012; Rautio et al., 2015), whereas the catchment of the Kokemäenjoki River includes more lakes (Table 1). Water from the Kokemäenjoki River is used as source water for the Virttaankangas MAR site.

## 2.2 Virttaankangas esker

The Virttaankangas esker, located in south-western Finland is the site of the largest MAR site in Finland (Fig. 1). The esker is a part of the glaciofluvial Säkylänharju-Virttaankangas complex (Punkari 1980; Ehlers et al. 1995; Artimo et al. 2003), and it is known to have sub-surface kettle hole structures, which affect groundwater flow. The landform is divided into three units: 1. The lowermost part is a result of repeated deposition of subaqueous fans containing glaciofluvial sands and gravels (Artimo et al. 2003). 2. This is overlain by glaciofluvial sand and silt, and associated glaciolacustrine silt and clay deposits. 3. The

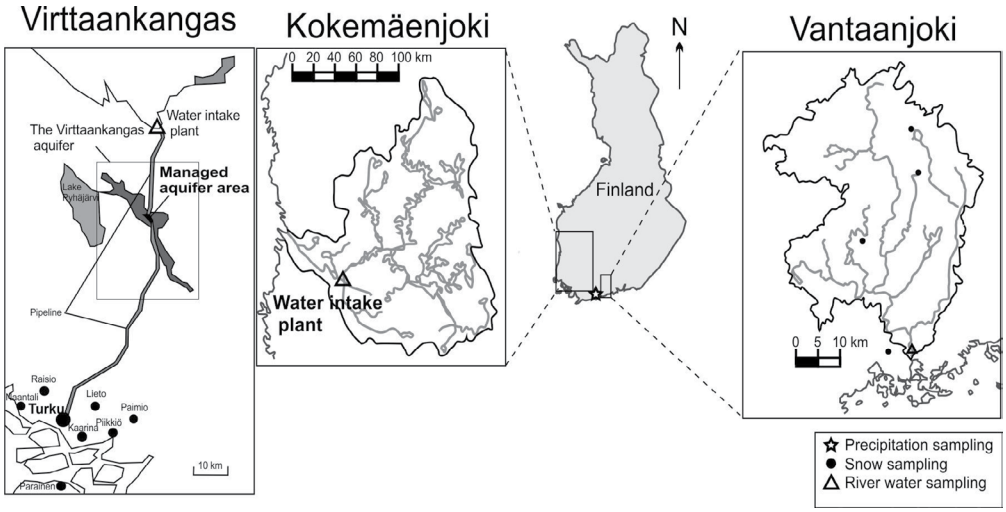


**Figure 1** Map showing the study areas of the Virttaankangas MAR site and the Kokemäenjoki and Vantaanjoki river catchments (modified after IAEA, 2013).

uppermost 10 - 20 m of the complex are littoral sands and gravels formed by the regression of the water level in the Baltic Basin 11 000 – 10 500 years ago (Artimo et al. 2003). Calcite is known to exist in the two lowermost units of the esker. In the finest <0.2 mm fraction the contents of calcite is 3.7 - 5 weight-%, which corresponds to 0.5 - 1.4 weight-% in the total sediment (Kortelainen et al., 2007). The $\delta^{13}C$ value of the calcite is -4.8 ± 0.5‰ (Kortelainen et al 2007). Calcite dissolution elevates the pH of natural groundwater to 8 - 9 or even 9.5 (Kortelainen & Karhu 2009).

# 3. Methods

## 3.1 Sampling

### 3.1.1 Precipitation collection

The isotopic composition of oxygen and hydrogen in precipitation was collected and analyzed for monthly samples at the Espoo GNIP station, southern Finland, from November 2000 to February 2012. In total, 135 monthly samples were collected according to the International Atomic Energy Agency (IAEA) guidelines. The isotopic composition of precipitation has been submitted to the Global Network of Isotopes in Precipitation database managed by the IAEA (IAEA, 2015).

Samples from snow cover were collected in March 2013 at nine different sites in Finland. In order to obtain samples representative of the whole snow cover at the sample localities, a cross-section of the snow cover was collected. The samples were packed in plastic bags and melted in the laboratory. After melting, the resulting water was analyzed for the isotopic composition of oxygen and hydrogen.

### 3.1.2 River water sampling

The sampling locations are listed in papers I and III. Oxygen and hydrogen isotope ratios were analyzed from all samples, and the isotopic composition of DIC, alkalinity and pH from all river water samples. The mean volume of discharge of the rivers was taken from the HERTTA database, maintained by the Finnish Environment Institute (SYKE, 2012).

**Table 2.** Phases of the startup of the managed aquifer recharge facility at Virttaankangas.

| Phase | Infiltration rate $m^3$/day | Duration |
|---|---|---|
| 0 | Natural groundwater circulation (31000 $m^3$) | |
| I | 20000 | September 2010 - October 2011 |
| II | 45000 | November 2012 - December 2013 |
| III | 65000 | March 2014 - August 2014 |

### 3.1.3 Groundwater sampling

The different phases of the MAR site are detailed in Table 2. The first part of the sampling for this study was executed during Phase I, the second part in Phase II and the third part in Phase III (Table 2). Altogether, 200 samples were collected for chemical analysis, and 162 samples for isotopic analysis. The sampling locations are presented in Paper II. The isotopic composition of local natural groundwater was monitored during 2007-2015.

## 3.2 Analysis

### 3.2.1 Isotope analysis

The samples for oxygen and hydrogen isotope analysis were collected in 50 mL HDPE plastic bottles which were entirely filled up, leaving no air space. The isotope ratios of oxygen and hydrogen were analyzed by a Picarro cavity ring-down spectrometer (CRDS) in the Department of Geosciences and Geography at the University of Helsinki, and at the Geological Survey of Finland. In both facilities, laboratory standards were calibrated against two international reference standards (VSMOW and SLAP). The accuracy of the analyses was 0.1‰ and 0.5‰ for oxygen and hydrogen, respectively.

DIC isotope samples were analyzed at the University of Helsinki, Department of Geosciences and Geography. The 5 mL samples were injected into helium filled Exetainer tubes which contained eight drops of 85% phosphoric acid, using 0.8 and 0.2 μm Supor membrane filters. The samples were analyzed by isotope-ratio mass spectrometry (IRMS), using a Thermo Finnigan Delta Advantage mass spectrometer. Laboratory standards, which have been calibrated against an international standard (NBS19) were used. The precision for the analysis was 0.1‰.

The isotopic composition of DOC was measured from two samples of the infiltrated water at the University of Jyväskylä. Freeze-dried water samples were incubated in HCl fume at room temperature for 16 hours, after which they were kept in desiccator until 0.5 mg of the samples was weighed in tin cups and analyzed with Thermo Finnigan DELTA plus Advantage IRMS and run against IAEA CH3, NBS-19 and the fish muscle carbon standards in the University of Jyväskylä isotope laboratory. The standard deviation between replicates was within 0.2‰.

### 3.2.2 Chemical composition

For the Virttaankangas groundwater samples, temperature, pH and dissolved oxygen were measured in the field using an YSI water quality meter equipped with 6562 Rapid Pulse Sensor (dissolved oxygen, precision ±0.2 mg/L), pH 6561 sensor (±0.2) and a temperature sensor

(±0.15˚C). The contents of DOC were analyzed in the field with S-CAN meter, with a precision of 1% and in the Labtium Oy laboratory by using the method described by the standard SFS-EN 1484, with a precision of ±20% and a 0.4 mg/L detection limit.

The samples for the alkalinity and pH measurements from the Vantaanjoki River were collected in plastic bottles and analyzed during the same day using an automatic titrator Schott Titroline alpha with accuracy of 0.003 mmol/L. The DIC contents and partial pressure of carbon dioxide ($pCO_2$) were calculated from alkalinity and pH using the geochemical modelling program PHREEQC (Parkhurst and Appelo 2013). The samples from the Kokemäenjoki River and the groundwater at Virttaankangas were analyzed for alkalinity and the concentrations of calcium, potassium, sodium, magnesium, chloride, nitrate and sulfate by Lounais-Suomen Vesi- ja ympäristötutkimus Oy (Water and Environment Research of Southwestern Finland Ltd.). The concentration of silica was measured by The Water Protection Association of the River Kokemäenjoki.

### 3.3 Modelling

#### 3.3.1 Groundwater flow model

The flow model was constructed using the MODFLOW 2005 code (Harbaugh et al., 2005). The modelling program used was Processing Modflow for Windows (PMWIN: Chiang and Kinzelbach 1991; 1993), and the code Modpath (Pollock, 2012). The details of the model are given in Paper II.

#### 3.3.2 Geochemical modelling

The amount of DIC and the speciation were modelled using PHREEQC from the measured pH and alkalinity of the water samples (Parkhurst and Appelo, 2013). Quantifying oxidative decomposition of DOC was achieved by inverse modelling using PHREEQC (Parkhurst and Appelo, 2013). The basic procedure of the inverse modelling used is described in Paper II.

## 4. Summary of original publications

### 4.1 Paper I

In Paper I, the Vantaanjoki and Kokemäenjoki rivers were studied using the stable isotopes of oxygen and hydrogen in river water. For comparison, the isotopic composition of oxygen and hydrogen in local precipitation was also measured. The aim of the study was to determine the sources of river water, whether the river was dominated by base or surface flow, and to make estimates about the mean residence time of the young surface flow component in river water.

Sinusoidal functions were fitted to the annual variations in the isotopic composition of river water and precipitation. These sinusoids were used to determine the mean residence time of the youngest surface flow component in the rivers. As groundwater in the area lacks these sinusoidal changes, the age of the groundwater could not be determined.

The mean residence time of the surface flow component in the case of the Vantaanjoki River was two months. Precipitation is detained in the snow cover from December until April, which corresponds to the mean residence time of the young component of the river. The Vantaanjoki River is basal flow dominated through most of the year, surface flow being the main component only during the spring flooding event caused by snow melt. However, the spring flooding season constitutes most of the annual discharge in the

Vantaanjoki River, thus it is predominantly a surface flow dominated river by volume.

It was deduced that the Kokemäenjoki River also has a substantial surface flow component, and also there the observed mean residence time reflects the surface flow component. Due to lake storage, the mean residence time of water in the catchment of the Kokemäenjoki River exceeds one year. The paper concludes that annual variability in the sources of water must be taken into consideration in MRT determination.

## 4.2 Paper II

In Paper II, the amount of dissolved organic carbon (DOC) and the onset of its decomposition in the managed aquifer recharge (MAR) site at Virttaankangas was established. The same sinusoidal fitting method was applied to resolve the mean residence time of artificially recharged water in observation wells. This knowledge, combined with the evidence from flow routes and shortest travel times of water, was used as an input to a 3D flow model made using MODFLOW.

After establishing the residence time of water in the aquifer, the consumption of calcite and the oxidative decomposition of dissolved organic carbon in the aquifer were modelled. It was concluded that calcite dissolution is practically instantaneous, whereas the decomposition of DOC depends on the residence time of water.

It was shown that microbial oxidative decomposition of DOC was delayed at Phase II of the MAR process, and could be quantified after the stabilization of the system in Phase III. The reason for the slow start of the process seemed to be the high pH of water. Calcite dissolution not only protects water lines from corrosion and prevents clogging of the aquifer, but also raises the pH of the water up to a value of 9 in a system closed to $CO_2$ exchange. The high pH was deduced to affect the decomposition of DOC either by providing a very different habitat for microbes or by affecting the chemical composition of the infiltrated water and thereby making it more difficult for the microbes to function efficiently. After the decomposition had started, it worked at least as efficiently as at other MAR sites. Based on the models, the amount of sorption was virtually nonexistent.

## 4.3 Paper III

In Paper III, the carbon contents of the Vantaanjoki River were examined. The isotopic composition of dissolved inorganic carbon (DIC), alkalinity and pH of the river water were analyzed. $pCO_2$ and the contents of DIC were calculated from the analytical data using the geochemical modelling program PHREEQC. The general aims of the study were to observe annual changes in the contents of DIC, to evaluate the overall quantity of DIC being transported and to evaluate the effects of human activities.

A significant part of the total flux of DIC in the river was found to be associated with spring flooding. By studying the isotopic composition of DIC, this carbon was sourced from soil respiration, which surface flow had flushed into the river channel.

Paper I demonstrated that water in the Vantaanjoki River has two different sources, with variable proportions in different seasons. Source variability was also reflected in the pH and DIC contents of the river water. The spring samples showed the characteristics typical of surface flow, whereas summer and winter samples had the characteristics of groundwater. Fall samples were located between these two end-members. These results correspond well with the results in Paper I. Anthropogenic effects were minor. The $pCO_2$ of the river water remained higher than that of the atmosphere throughout the flowpath

and throughout the year. Thus the river acts as a carbon source for atmospheric $CO_2$ rather than as a sink.

# 5. Discussion

## 5.1 Sinusoidal fitting and mean residence times (papers I and II)

Using the stable isotopic composition of oxygen in river and groundwater to resolve the MRT of water was first introduced by Stichler (1980) and was later on used by many to resolve MRT's in different river systems (Burgman et al., 1987; Dóša et al., 2011). This method is useful since the analytical techniques are simple and low cost, and the tracer occurs naturally in water (Kendall and McDonnell, 1998). All that is required is regular monitoring of river water and precipitation. Nevertheless, recent findings have shown that this method may exaggerate the age of river water and so the method may not be always applicable (Kirchner, 2015). This is due to mixing of waters from different sources with different isotopic signals.

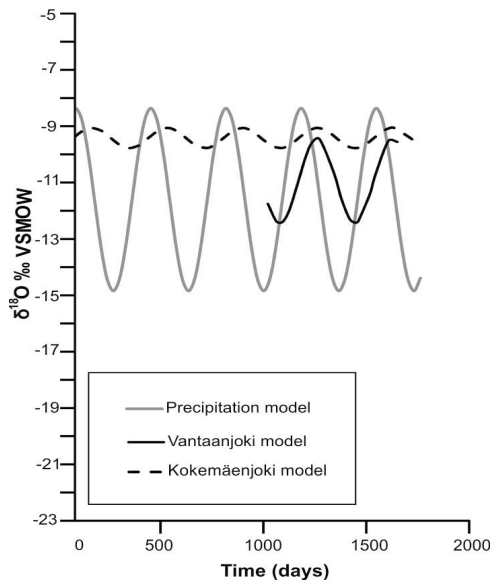


**Figure 2.** Sinusoidal functions were fitted to the isotopic composition of oxygen ($\delta^{18}O$) in precipitation and the water in the Vantaanjoki and Kokemäenjoki rivers.

We studied two cases where the method has the potential to be applicable despite its limitations. In Paper I, we studied two rivers with distinct spring flooding events. Both displayed a clear sinusoidal signal in the isotopic composition of oxygen (Fig. 2). From this and the precipitation data MRT's were calculated using both the amplitude damping and the phase shift, and they seemed to be consistent: for the Vantaanjoki River the MRT was 2 months, for the Kokemäenjoki River with a larger lake volume, the MRT was 14 months (Paper I).

The two months MRT for the whole water body in the Vantaanjoki River is not consistent with the previous finding by Korkka-Niemi et al. (2012) and Rautio et al. (2015) suggesting a significant base flow component. The two month MRT is, however, consistent with the mean residence time of snow in southern Finland, the first snow falling in December and the last remains melting in April. The addition of basal flow into the river channel must increase the MRT of the water, since the residence time of the groundwater in the area is long enough that the seasonal variations in the isotopic composition could not be detected (Kortelainen and Karhu 2004).

The isotopic composition of the snow cover (Table 3) is almost directly transferred into the river water creating the most negative $\delta^{18}O$ values of the year (Fig. 2). During the snow melt season, the base flow component in the river water is negligible. The discharge during the spring flooding can amount to as much as 70% of the whole annual discharge (SYKE 2012), which also makes it the most prominent feature in the isotopic composition of the river water and it therefore dictates the MRT.

In the special case of the Vantaanjoki River, where most of the annual discharge is actually

sourced in the spring flooding, even though the river is base flow dominated other times of the year, it can be concluded that the MRT represents the MRT of the snow cover in the region. For the Kokemäenjoki River, no such conclusion can be made, since its isotopic composition is strongly affected by storage in numerous lakes and associated evaporation.

A special situation, where the isotopic composition of oxygen can be used to determine the MRT correctly, is MAR. In MAR, surface water is infiltrated into the soil by different methods (Dillon 2005; Page et al. 2009; Dillon et al. 2009). Since there is usually only one external water source and one direction of flow, the system is simple enough to estimate the MRT from isotopic measurements (Paper II). The only requirements are, that the source water itself still manifests the sinusoidal behavior inherited from precipitation, and that the MRT is not longer than one year. The latter is due to the fact that the amplitude damping method cannot be utilized, as mixing with natural groundwater dampens the signal, and the phase shift method can only differentiate between MRT's of less than a year (Clark and Fritz 1997). In the case of the MAR site at Virttaankangas, these conditions were true for three of the four production wells studied (Paper II). The fourth well had continuously evolving isotope ratios indicating that the proportion of infiltrated water was increasing. Here seasonal cycles were obscured, and modelling was not attempted.

## 5.2 Groundwater - surface water proportions (papers 1 and 3)

In previous studies, the amount of base flow in the Vantaanjoki River has been studied using stable isotope compositions and silica contents (Rautio et al., 2015), as well as thermal imaging (Korkka-Niemi et al., 2012). Even though the influence of base flow was evident in these studies, the results were difficult to interpret quantitatively.

In regions where lakes and rivers are seasonally covered with ice and precipitation falls as snow during the cold season, it may be possible to determine the proportion of groundwater in a surface water body. This is possible, because surface flow is non-existent, and evaporation effects are negligible. This was successfully achieved in the case of the Vantaanjoki River, yielding 63% of the river

**Table 3.** The isotopic composition of snow samples from the catchment of the Vantaanjoki River.

| Location | Date | $\delta^{2}H$ ‰VSMOW | $\delta^{18}O$ ‰VSMOW |
|---|---|---|---|
| Nurmijärvi | 2.4.2013 | -116 | -15.8 |
| Hyvinkää | 29.3.2013 | -114 | -15.7 |
| Kumpula | 1.4.2013 | -98 | -13.6 |
| Kannelmäki | 31.3.2013 | -103 | -14.2 |
| Rajamäki | 8.4.2013 | -113 | -15.3 |
| Mean | | -109 | -14.9 |
| Stdev | | 8 | 1.0 |

water having been originated from groundwater during the cold winter months (Paper I). This was perceived to be the maximum amount of base flow to the river. The minimum amount of base flow is present during the spring flooding event, since the isotopic composition of oxygen in the river water is, within error limits, the same as that in the snowmelt (Table 3).

For the summer and autumn months, only indirect ways of examining the base flow influence exist. These include the different DIC contents of the river water with respect to surface flow. Base flow usually has a higher DIC concentration than surface flow, having collected carbon originating from soil respiration during infiltration (Doctor et al. 2008; van Geldern 2015). Precipitation has very low DIC concentration (Stumm and Morgan 1996).

In the catchment of the Vantaanjoki River, it was found that surface flow has lower pH and lower DIC contents than those in base flow (Paper III) and these differences could be used to evaluate distinct water sources. The proportion of base flow must be larger in the summer than that in the autumn (Fig. 3a), which corresponds to higher discharge in the fall, brought by added precipitation (SYKE 2012).

The carbon balance of the river is strongly affected by base flow - surface flow proportions (Fig. 3a). However, it is not possible to contribute all variation in the carbon balance of the river water to changes in the surface water - base flow ratio. In the summer, the relative amount of base flow is high, but the isotopic composition of DIC is more depleted in $^{13}C$ compared to the spring or autumn, with higher surface flow proportions. Throughout the year, the $\delta^{13}C_{DIC}$ values of water in the Vantaanjoki River are considerably higher compared to those in groundwater (Paper III). Therefore, other factors must be involved in addition to base flow and surface flow. Since the $pCO_2$ in the river is higher than in the atmosphere, the most likely explanation for these changes is $CO_2$ degassing (Fig. 3b). Even though photosynthesis can cause similar effects, it is not likely that there is a significant amount of photosynthesis taking place in the river channel due to the short MRT of the river water. Human induced changes are local and temporal and do not have a large effect on the inorganic carbon balance of the river water.

## 5.3 Following the MAR process (paper II)

Comparing the mean residence time (MRT) and the shortest travel time (STT) of the artificially recharged water at the MAR site in Virttaankangas revealed that the residence times given by a flow model and those provided by

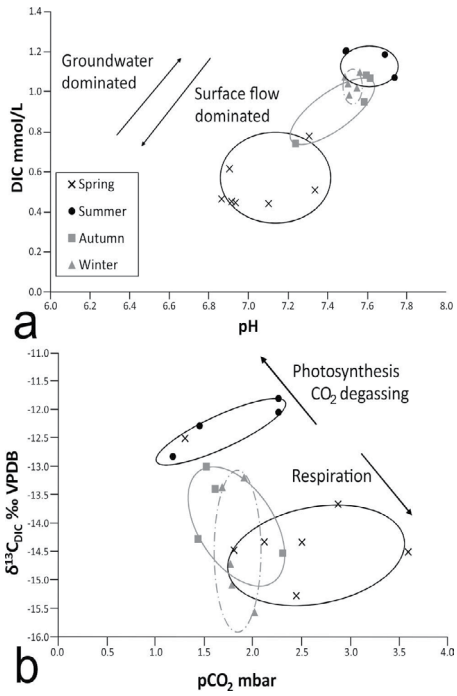


**Figure 3.** A. Differences between surface flow dominated spring samples and groundwater dominated summer samples are portrayed with respect to pH and DIC. B. Differences between $CO_2$ degassing / photosynthesis and respiration signals in $pCO_2$ and $\delta^{13}C_{DIC}$ (modified after Paper III).

stable isotope tracers are not necessarily equal. MRT describes better the amount of time the water spends in the aquifer, whereas STT describes the time when the first signs of infiltrated water can be found in the well in question (Paper II). Flow modelling provides good estimates for the STT of the river water; however, the MRT is best estimated from the isotope sine fitting method. A longer STT does not always correspond to a longer MRT. The latter is, however, linked to the amount of oxidative decomposition of DOC (Fig. 4), and, therefore, it is a useful parameter for an MAR facility. Paper II demonstrated clearly that the amount of DOC decomposition rises with a longer MRT.

At the Virttaankangas MAR site it was possible to verify the onset time and the amount of DOC decomposition using PHREEQC modelling (Parkhurst and Appelo 2013) Specifically, modelling quantified the effects of the dissolution of trace calcite present in the aquifer on the basis of isotope mass balance calculations. The modelling program was also shown to be an excellent tool for monitoring the amount of DOC decomposition in a setting where several sources affect the DIC contents of water. Adding carbon isotope data to modelling increased the accuracy. However, to further understand and quantify the operation of MAR further knowledge on the microbial community

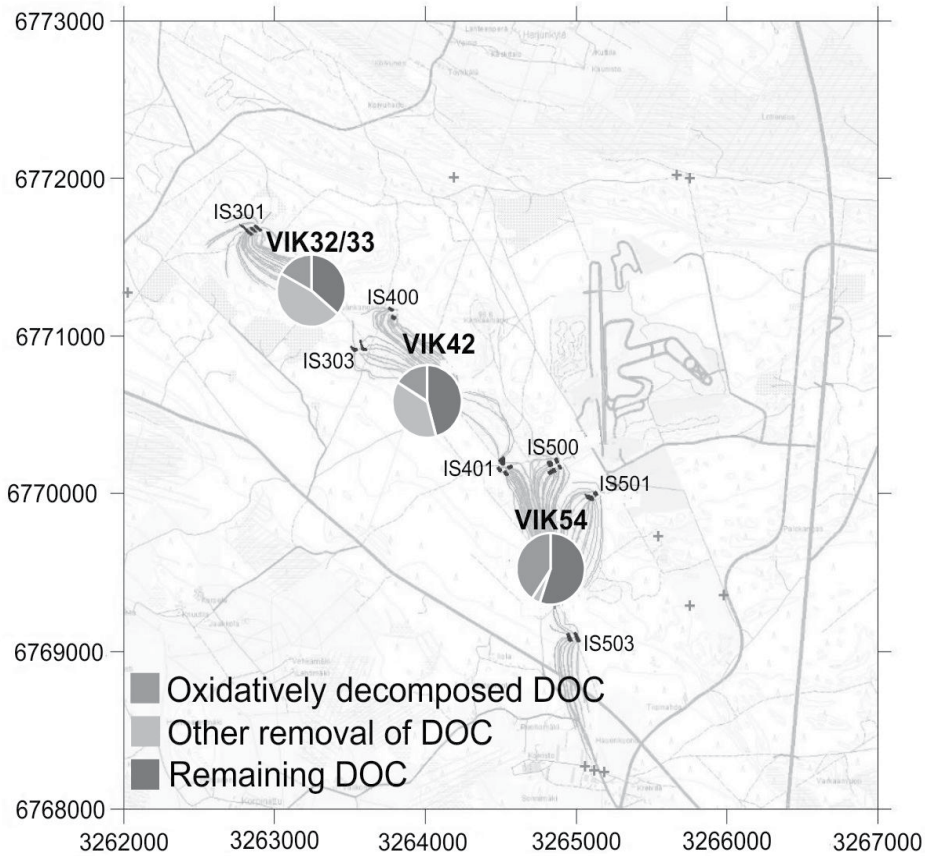


**Figure 4.** Map showing the infiltration areas and flow directions, as well as the amount of oxidatively decomposed dissolved organic carbon (DOC) and other removal, either the effect of sorption or mixing with natural groundwater. In the case of VIK32/33 the mean of the different amounts of decomposition has been used.

present in the Virttaankangas aquifer is required.

At the Virttaankangas MAR site, carbonate weathering reactions increase the pH of the recharged water to 8 - 9.5 (Kortelainen and Karhu 2009). These high pH values possibly affect chemical reactions and the microbial community in water. Two major differences to MAR sites with a pH close to neutral could be detected (Greskowiak et al. 2005; Vanderzalm et al. 2006; Kolehmainen et al 2009; 2010; Graham et al. 2015). In high pH environment: 1. Oxidative decomposition of DOC was delayed in the beginning of the operations, and 2. The proportion of decomposition was high compared to sorption. The processes behind these differences seem to be related to pH, but require further investigation.

### 5.4 Implications for future research

Finding reliable and feasible methods to determine mean residence time of surface and groundwaters, and to quantify groundwater - surface water interaction requires further study. In simple systems, the stable isotope composition of water can be used satisfactorily to resolve some of these questions, but the limitations of the methods need to be better constrained. Since isotope analyses of hydrogen and oxygen are relatively low-cost methods, they remain the best practical method to determine and quantify MRT and groundwater-surface water interaction.

The isotopic composition of DIC can be used in various ways to resolve the origin of DIC and to investigate processes affecting the carbon balance in surface and groundwaters. In this study, the focus was on seasonal cycles and trends, and the temporal sampling density did not allow to make any inferences about the diurnal cycles of photosynthesis and respiration.

The effect of pH on the MAR process remains partly unresolved. In further investigations, also microbial analysis techniques should be applied to get information on the evolving microbial community. The Virttaankangas site is special, not so much for its carbonate contents, but for the capability of trace calcite to raise the pH of water. This undoubtedly has an effect on the MAR process clearly requiring further research.

## 6. Conclusions

1. Annual isotope variations in precipitation can be used to determine MRT only under special circumstances. An example is a system consisting of water from one source showing a regular seasonal isotope variation curve. This requirement could be fulfilled, for example, in an MAR system. In areas where precipitation during the cold season is stored as snow leading to a distinct spring flooding event, the phase shift method shows the residence time of the snow cover. In general, defining the MRT of a river system is not possible by this method, because of unknown quantities and ages of the base flow component and the effects of lake storage.

2. Isotope mass balance can be applied to estimate mixing of different water bodies. The method requires that the components have distinct isotopic signatures. The groundwater - surface water ratio in river water can be estimated using isotope mass balance calculation based on $\delta^{18}O$ or $\delta^{2}H$. In the case of the Vantaanjoki River, the base flow component was estimated to be 63% of the total flow during the winter. During the spring flooding event, the river water was 100% surface flow. From the carbon contents of the water it could be deduced that summer samples contained more base flow than the fall ones, but precise proportions could not be determined.

3. $\delta^{13}C_{DIC}$ can be applied to study surface flow – base flow interaction in a river catchment. In the case of the Vantaanjoki River, groundwater

influence could be clearly seen in the DIC contents and the pH of the water, and the summer and winter flows could be clearly differentiated from the spring flow based on these parameters. In the fall, the composition of water was characterized with values intermediate compared to other seasons. The isotopic composition of DIC mostly indicated base flow originated DIC, with some $CO_2$ degassing into the atmosphere.

4. Oxidative decomposition of DOC in MAR can be monitored using $\delta^{13}C_{DIC}$. In a complex environment with other carbon sources, supporting geochemical modelling is required. It was possible to pinpoint the onset and the quantity of oxidative decomposition of DOC by geochemical modelling, the accuracy of which was greatly enhanced by isotopic data. The beginning of the oxidative decomposition of DOC was observed to be delayed in a high pH environment, but once it had commenced, it was proven to be at least as efficient as at other MAR sites with close to neutral pH conditions. The amount of sorption was negligible compared to the amount of decomposition.

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